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Hydrodesulfurization of Dibenzothiophene Catalyzed by Silica-Alumina Supported Anionic Molybdenum Carbonyl Complexes

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In hydrodesulfurization (HDS) of dibenzothiophene (DBT), the catalysts prepared from silica-alumina supported molybdenum compounds showed higher yields of biphenyl, cyclohexylbenzene and bicyclohexyl than conventional sulfided molybdena-alumina. Specifically, the catalysts derived from silica-alumina supported anionic molybdenum carbonyls gave the highest yields among silica-alumina supported ones.

Although supported metal carbonyl complexes are found to be active for several catalytic reactions,1) e.g. hydrogenation of carbon monoxide, metathesis of olefin, etc., their reactivities for hydrodesulfurization (HDS) of thiophenes have been scarcely investigated. There are only a few examples where thiophenes were desulfurized by catalysts derived from supported-$Mo(CO)_6$2) and $Ru_3(CO)_{12}$.3) On the other hand, it has been well-known that DBT would be one of key compounds in deep HDS of heavy feedstock, e.g. light oil.4) To our knowledge, however, there was only little literature for HDS of DBT catalyzed by supported metal carbonyls.5) Recently, we have reported that the catalysts derived from hydrogenolysis of alumina-supported anionic molybdenum carbonyls are more effective for HDS of DBT than conventional sulfided MoO_3/Al_2O_3.6)

In the course of our study, we investigated the effect of supports on HDS of DBT catalyzed by supported molybdenum carbonyl complexes. We report here that silica-alumina supported catalysts reveal much higher catalytic activity than those derived from alumina-supported molybdenum carbonyls and a conventional molybdena-alumina. Further, it has been found that the catalysts derived from silica-alumina supported anionic molybdenum carbonyls give much higher yields of biphenyl (BP), cyclohexylbenzene (CHB) and bicyclohexyl (BCH) than silica-alumina supported conventional one.

Commercially available $Mo(CO)_6$, triethylamine (NEt_3), ethanethiol (EtSH), and xylene were used without further purification. Tetrahydrofuran (THF) was distillated from sodium benzophenone ketyl. SiO_2-Al_2O_3 was supplied from Catalysis Society of Japan (JRC-SAL2: 560 m^2/g) dried under vacuum at 350 ^oC. $[NEt_4][Mo(CO)_5(OOCCH_3)]$ was synthesized by reported method.7) The $Mo(CO)_6$-NEt_3-EtSH/SiO_2-Al_2O_3 system was prepared as follows: 0.11 g of $Mo(CO)_6$ was added into a 50 mL reactor and was dissolved in THF (10 mL). The solution was stirred and exposed to UV irradiation under reflux for 2 h to give $Mo(CO)_5THF$8) which reacted with NEt_3 (0.084 g) and EtSH (0.052 g) at room temperature to give dark brown solution. This solution showed the IR absorptions at 1941(very strong) and 1871(medium) cm^{-1} which was due to the formation of $[NEt_3H][Mo_2(CO)_{10}SEt]$.9) 0.46 g of SiO_2-Al_2O_3 was added into the solution.

Table 1. Hydrodesulfurization of Dibenzothiophene Catalyzed by Silica-Alumina Supported Molybdenum Catalysts a)

Run	Catalyst	Conv. of b) DBT %	Conv. of DBT to BP %	Conv. of DBT to CHB %	Conv. of DBT to BCH %	Rate c) of HDS (mol/mol-Mo/h)	Mo content wt%
1	$Mo(CO)_6/SiO_2$-Al_2O_3	31(26)	17	7	2	0.42	5.3
2	$[NEt_4][Mo(CO)_5(CH_3COO)]$ $/SiO_2$-Al_2O_3	85(58)	26	28	4	0.71	7.0
3	$Mo(CO)_6$-EtSH-NEt_3 $/SiO_2$-Al_2O_3 d)	46(46)	40	5	1	0.58	6.8
4	$Mo(CO)_6$-EtSH-NEt_3 $/SiO_2$-Al_2O_3	79(56)	22	27	7	0.74	6.5
5	MoO_3/SiO_2-Al_2O_3 e)	91(39)	19	11	9	0.49	6.8
6	MoO_3/Al_2O_3 e,f)	38(38)	27	11	-	0.40	7.8

a) Reaction temp. 300 °C, Pressure 50 kg/cm^2, WHSV 16.5 h^{-1}, Cat. 0.50 g, H_2 18 L/h; Initial concentration of DBT 1.0 wt%. Presulfided by H_2S in H_2 at 350 °C (H_2S 3%). b) Total conversion of DBT. The sum of the conversions of DBT into BP, CHB, and BCH, which represents the conversion of DBT by HDS, is given in parenthesis. The difference between the total conversion and the value in parenthesis represents the conversion of DBT by hydrocracking. c) Rate of HDS of DBT into BP, CHB, and BCH. This value was calculated from the sum of the conversions of DBT into BP, CHB, and BCH. d)Activated by H_2 stream at 350 °C. e) Reaction Temp. 300 °C, Presulfided by H_2S in H_2 at 400 °C (H_2S 3%). f) Surface area of alumina: 274 m^2/g.

After the mixture was stirred for 2 h, THF was removed in vacuo. MoO_3/SiO_2-Al_2O_3 was prepared by conventional method. A catalyst precursor was placed into a pressurized fixed-bed flow reactor (10 mm I.D. x 300 mm), heated at 5 °C/min and activated at 300 °C under a flow of H_2 or 3% H_2S/H_2 (30 mL/min) for 2 h. When conventional MoO_3/SiO_2-Al_2O_3 was used, presulfidation was performed at 400 °C for 3 h. HDS of DBT was carried out under the following conditions: 300 °C; 50 kg/cm^2; H_2 18 l/h; WHSV, 16.5 h^{-1}; initial concentration of DBT, 1.0 wt%; catalyst, 0.50 g. Reaction products were analyzed by gas chromatography. The molybdenum contents in used catalysts were measured by the absorbance analysis. Volumetric measurement of NO chemisorption was carried out in a conventional Pyrex glass high vacuum adsorption system. For infrared measurements, self-supporting wafers were placed in a special infrared cell which allowed to perform dynamic treatments of sulfidation and hydrogenation.

Catalysts derived from silica-alumina supported molybdenum carbonyl complexes were active for HDS of DBT over 10 h and major products for HDS were biphenyl (BP), cyclohexylbenzene (CHB) and bicyclohexyl (BCH). The results are shown in Table 1. When $Mo(CO)_6/SiO_2$-Al_2O_3 was presulfided by H_2S in H_2 (run 1), the conversion of DBT was 31%. When the anionic molybdenum complex $[NEt_4][Mo(CO)_5(OOCCH_3)]$ was supported on SiO_2-Al_2O_3 (run 2), the catalytic activity remarkably increased and the conversion of DBT reached 85%. Catalysts prepared by hydrogenolysis and presulfidation of the $Mo(CO)_6$-NEt_3-EtSH/SiO_2-Al_2O_3 system also revealed high catalytic activities (runs 3 and 4). Especially, the catalyst prepared by hydrogenolysis showed the high selectivity for BP (run 3). As shown in Table 1, the catalysts prepared from presulfidation of

Table 2. Characterization of Supported Molybdenum Catalysts by Means of NO Chemisorption.a)

Run	Catalyst	NO Chemisorption Wavenumber cm^{-1}		NO Adsorption (μmol/g-cat)	NO/Mo (mol/mol)
7	$[NEt_4][Mo(CO)_5(CH_3COO)]$ /SiO_2-Al_2O_3b)	1800	1707	170	0.23
8	$Mo(CO)_6$-EtSH-Et_3N /SiO_2-Al_2O_3c)	1806	1701	435	0.61
9	$Mo(CO)_6$-EtSH-Et_3N /SiO_2-Al_2O_3b)	1792	1698	160	0.24
10	MoO_3/SiO_2-Al_2O_3d)	1800	1711	129	0.18
11	MoO_3/SiO_2-Al_2O_3e)	1800	1707	347	0.49
12	MoO_3/Al_2O_3d)	1786	1688	110	0.14

a) All measurements of NO chemisorption were carried out at 25 °C. b) Presulfided by H_2S in H_2 at 350 °C (H_2S 3%) for 2 h and evacuated at 350 °C for 2h. c) Activated by H_2 at 350 °C for 2 h and evacuated at 350 °C for 2 h. d) Presulfided by H_2S in H_2 at 400 °C (H_2S 3%) for 3 h and evacuated at 400 °C for 2 h. e) Presulfided by H_2S in H_2 at 400 °C (H_2S 3%) for 3 h, treated with H_2 at 400 °C for 2 h and evacuated at 400 °C for 2 h.

silica-alumina supported anionic molybdenum complexes showed the higher rates of BP, CHB, and BCH formation per the content of molybdenum and the higher selectivity for CHB (runs 2 and 4).

In the catalyst derived from presulfidation of a conventional MoO_3/SiO_2-Al_2O_3 (run 5), the conversion of DBT reached 91%. However, the yields of BP, CHB, and BCH (the sum of the conversions of DBT into BP, CHB and BCH) and the rate of HDS of DBT into BP, CHB,and BCH per the content of molybdenum were much lower than those in runs 2 and 4. This indicates that the hydrocracking of the significant amount of DBT occurred on the catalyst derived from MoO_3/SiO_2-Al_2O_3. Benzene and toluene were mainly detected by GC analysis as products for hydrocracking. Because benzene and toluene can be also formed from solvent xylene, however, the amounts of these products formed by hydrocracking of DBT have not been determined in the present time. When the catalysts derived from silica-alumina supported molybdenum carbonyls were used (runs 1-4), the conversion of DBT by hydrocracking was much less than that in the case of MoO_3/SiO_2-Al_2O_3. Although the hydrocracking of DBT hardly occurred with the use of alumina-supported molybdenum carbonyls6) and molybdena-alumina (run 6), the rates of HDS of DBT into BP and CHB were much lower than those of silica-alumina supported anionic molybdenum carbonyls and were very close to that of MoO_3/SiO_2-Al_2O_3.

Characterization of silica-alumina supported molybdenum catalysts was performed by means of FTIR and NO chemisorption. After hydrogenolysis or presulfidation of these catalyst precursors, NO chemisorption was measured and the results are shown in Table 2. Both the wavenumber and the amount of NO chemisorption for sulfided MoO_3/Al_2O_3 (Run 12) were in good agreement with those reported by other workers.10) The wavenumbers of the doublet peak were 1786 and 1688 cm^{-1}, which are assigned to dinitrosyl species adsorbed on the edge of MoS_2. The wavenumbers and the shapes of peaks of silica-alumina supported catalysts were very close to those of sulfided MoO_3/Al_2O_3. Therefore, the catalysts prepared from sulfidation of silica-alumina supported molybdenum carbonyls (runs 7-9) can be deduced to have similar structure of active species. The amounts of NO adsorption for catalysts derived from silica-alumina supported molybdenum carbonyls were larger than those for sulfided MoO_3/SiO_2-Al_2O_3 (run 10) and MoO_3/Al_2O_3 (run 12). Further, the amount of NO adsorption for the catalyst prepared from hydrogenolysis of the supported molybdenum carbonyl (run 8) was much larger than those for sulfided ones (runs 7 and 9) and that for one prepared by hydrogen treatment of sulfided MoO_3/SiO_2-Al_2O_3 (run 11). These results indicate that, at the preparation of catalysts, the catalysts derived from supported metal carbonyls have higher dispersion of molybdenum species than the conventional ones. Figure 1 shows the relationship between the amount of the NO adsorption and the rate of HDS of DBT into BP, CHB, and BCH. When the amount of the adsorbed NO per molybdenum loaded increased, the rate of HDS linearly increased. NO chemisorption seems to reflect the number of active sites for HDS as well as the surface coverage or dispersion of Mo.

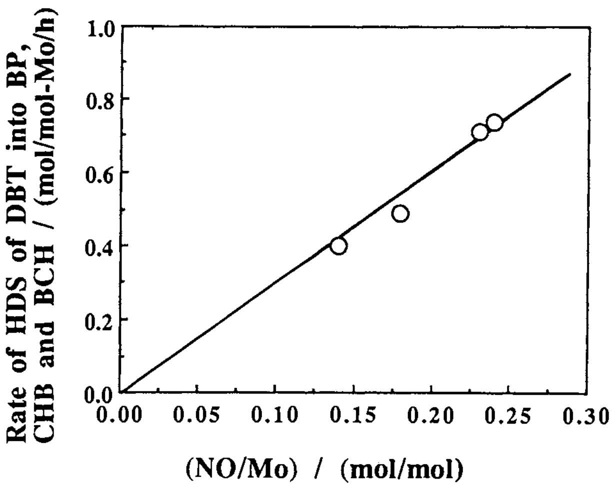

Fig. 1. The relationship between NO/Mo ratio and the rate of HDS of DBT into BP, CHB, and BCH. Data for runs 2, 4, 5, and 6 in Table 1 and runs 7, 9, 10, and 12 in Table 2 were used.

Clausen et al. reported in the study of sulfided MoO_3/Al_2O_3 using EXAFS that Mo was predominantly present as MoS_2-like domains.11) It has been also proposed that the adsorption of NO occurred mainly on Mo atoms present as MoS_2.10) In our systems, it is likely that MoS_2 highly dispersed on silica-alumina is formed by sulfidation of silica-alumina supported anionic molybdenum carbonyls.

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